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(54) Title: COMPLEX ADMIXTURE AND METHOD OF CEMENT BASED MATERIALS PRODUCTION**(57) Abstract**

The present invention relates to admixtures production and to method of the admixtures application in cement and concrete technology. The method allows to produce high-strength and high durable cement based systems, as well as cement systems with specially designed properties or cheap high-volume mineral admixture cements.

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COMPLEX ADMIXTURE AND METHOD OF CEMENT BASED MATERIALS PRODUCTION

BACKGROUND OF INVENTION

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1. FIELD OF THE INVENTION

The present invention relates to admixtures production and to method of the admixtures application in cement and concrete technology. The method allows to produce high-strength and high durable cement based systems, as well as cement systems with specially designed properties or cheap high-volume mineral admixture cements.

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2. DESCRIPTION OF THE PRIOR ART

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The admixtures for cement systems, especially high range water reducers or superplasticizers, have significant influence on strength and durability of concrete due to ability to reduce water demand and provide low porosity and permeability. The usage of such admixtures allows to produce concrete with high level of properties. The application of new high range water reducing agents for production of ultra high-strength concrete is explained in some US patents (US Pat. 5,466,289). Advantages of the high strength and high durable concrete have provided their large-scale applications in construction projects such as high-rise buildings, bridges, marine and offshore structures, tunnels, parking desks, repairing of structures, etc.

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There are many products marketed as high range water reducers for concrete. The original composition of high range water reducers is protected by numbers of International patents (for instance, in US Pat. 5,584,920; 5,494,516;

5 4,704,415; 4,460,720 and 4,441,929) and it is well-known that essentially they are
lignosulphonates-, melamine-, naphthalene- and polyacrylate- based compounds.
The process of water reducers production is realised in aqueous solution and the
final product contains 55 - 75 % of water. Application of water reducers in
aqueous solution is impossible for some dry production process, such as cement
10 and dry mortar. Usage of dry or semi- dry water reducers is more attractive for
ready mix and precast concrete plant or construction site due to the reason of easy
transportation and storage. For such projects dry powder water reducers are
available. Production cost of the powder admixtures rises up to two times because
drying process in special apparatus is used to remove water. Development of the
15 cheapest process for the dry- or semi- dry water reducing admixtures would be
useful to extend the frames of their application.

Process explained in US Pat. 4,297,309 (except final procedure of firing)
that allow to produce articles with different shape based on fine silica particles and
water is very close to present invention. Application of active calcium reactive
20 sorbents for combining of some gas and liquid chemicals, especially for sulfur
dioxide and metals, is also described in some US patents (US Pat. No 5,405,535;
5,227,351). Usage of invented complex admixture in cement and concrete
technology is similar to existing mode for mineral admixtures such as fly ash (US
Pat. No 5,601,643) application.

25 The main difference of the present invention is ability to create economical
combinations in sorbent - water reducer system that can be used as universal and
super effective modifiers for cement systems. The available test results confirm
that synergetic effect of sorbent - water reducer is multiplied in case of increasing
of preliminary treatment of cement - invented modifier compositions in dry or
30 liquid state. This advantages allow to achieve new level of properties or provide
production of wide range of new and more economic cement based materials with
conventional properties.

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SUMMARY OF THE INVENTION

The present invention is directed to development of the dry and semi- dry admixtures composition and production process. The usage of active silicon dioxide based sorbents allows to combine water containing in water reducers and to produce new complex admixture for modifying of cement system. The main criterion of sorbents selection is compatibility with cement system, especially for long- term action. The correct combinations in sorbent - water reducer system allows to create wide range of universal and super effective modifiers for cement systems.

The method of the complex admixture application in cement and concrete technology allows to produce the high-strength and high durable cement based systems, as well as the cement systems with specially designed properties or cheap high-volume mineral admixtures cements. The method is based on modification of cement or dry mix in production process by invented complex admixtures. This allows to increase the compressive strength of cement based materials up to 145-180 MPa and/or to introduce a large quantity of mineral indigenous admixtures up to 70% in the cement composition.

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DETAILED DESCRIPTION OF THE INVENTION

The dry or semi- dry complex admixtures production process includes mixing of water reducer solution with powder components of active sorbents.

The most important component of the sorbent is presented by fine alkali reactive silica dioxide based materials. Virtually any composition that includes fine or superfine non-crystalline silica dioxide may be applied in the practice. Such compositions include, but are not limited by fly ash, rice husk ash, zeolite, silica fume, bentonite, activated kaolin, montmorillonite, diatomaceous earth, etc.

- 5 The mass ratios of reactive silica dioxide component to water reducer ranging from about 5:1 to about 100:1 are preferred.

Available high range water reducers, as well as their mix (including other admixtures) can be used. The best results are achieved in case of sulphonated melamine (SMF) or naphthalene (SNF) formaldehyde, as well as polyacrylate
10 (PA) based high range water reducer application. The water content of high range water reducer component can be varied from about 25 to about 85 %.

The high porous lightweight sand (with particles size less than 5 mm) can be used as water accumulating component of active sorbent. The wide range of natural and artificial lightweight materials, as volcanic pumice, tuff, expanded
15 clay, expanded perlite, expanded slag, expanded glass, etc can be used. The mass ratios of reactive silica to accumulating porous component can be varied from about 10:1 to about 1:1.

The non-organic or organic salts or hydroxides of metals can be used as electrolytic agent, which provide better distribution and dissolving of the complex
20 admixture particles in aqueous media. Such compositions include, but are not limited by metal (especially, alkali and alkali earth) aluminates, hydroxides and carbonates: sodium nitrite, sulphate Al, Na, K, Ca, calcium chloride, calcium formate, etc. The introduction of the electrolytic agent into process can be made before or together with reactive silica component mixing in order to provide better
25 homogenisation of system. The mass ratios of reactive silica component to electrolytic agent can be varied from about 10:1 to about 1000:1. Accelerating effect on cement hardening process can be achieved in case of the composition application.

The low-, hemi- and non- water salts or combinations that are able to
30 combine with water can be used to bond free water in the system. The water-combining component can be applied before, during or after mixing of the main composition. The last case provides the formation of the granules covered by dense protective layer. This solution may be very useful if total amount of water is high and due to some reasons reactive silica content can not be increased. The one

5 or more types of calcium sulfate, high alumina cement or sulphate Na can be used as water combining component. The mass ratios of reactive silica to water combining component can be adjusted from about 1:1 to about 100:1. The effect of regulation of cement setting time, as well as accelerating of hardening process can be achieved for such composition.

10 The complex admixture can contain water-soluble polymer, which can be applied at any time during the main composition mixing. The usage of dry or aqueous dispersion of polymer, as well as combination of several polymers is possible. The introduction of the water-soluble polymer after mixing of the main composition provides the formation of the stronger granules. Acrylic acid or
15 acrylic acid copolymers, polyvinyl alcohol, polyvinyl acetate, poly acryl amide, polyethylene oxide, cellulose ethers, methyl cellulose, carboxymethyl cellulose, hydroxyethyl cellulose can be applied in this composition. The mass ratio of reactive silica to water soluble polymer can be varied from about 3:1 to about 100:1. The usage of the complex admixtures containing water soluble polymer for
20 cement modification allows to produce the systems with desired rheological behaviour, for instance, reduce the cement paste viscosity at the certain time, increase pumping of fresh mortar and concrete, as well as to improve some strength characteristics, as tensile, flexural, impact and bond strength, modulus of elasticity, etc.

25 The composition can contain any retarders of hydration, setting, and hardening of cement system. The retarders include, but are not limited by lignosulphonates, sugars, hydroxycarbonic acids and their salts, carboxylates, phosphonic or phosphoric acids, as well as their ethers and salts. The mass ratio of reactive silica to retarder can be chosen from about 50:1 to about 1000:1. The
30 retarder application is more suitable for delaying of cement setting time, as well as for significant reduction of heat development.

The available air detraining, hydrophobic, air entraining, foaming and/or gas creating admixtures can be applied as component of the main composition. Three-butyl phosphate can be used as air detraining component. Silicon based

5 compounds containing silicones, silanes, silanols or siloxanes groups such as alkyl alkoxy silanes can be used as hydrophobic components. Air entraining and foaming agents can be neutralised hydroaromatic and fatty carboxylic acid, tall oil, vinsol resin and protein-based admixtures. The powder of some metals (for example, aluminium), as well as hydrogen peroxide can be applied as gas creating
10 admixture. The film and structure creating actions, as well as self- dissolving effects of these admixtures are used for production of well-performed complex products. The mass ratio of reactive silica to structure formation components can be varied from about 10:1 to about 10000:1. The usage of this kind of structure formation components provides necessary porous system of cement paste from
15 dense non-porous to cellular lightweight structure. The hydrophobic components provide creation of super thin hydrophobic layer on porous area surface. The gas creating agents can be used also for elimination of shrinkage, production of expanding cements or accelerating of hardening and heat development for production self- curing systems.

20 Grinding aids can be submitted as component of the main composition. The triethanol amine, amine acetate salts, EDTA, acetic acid, hydrocarbons, silanes, methyl chlorine or fluorine silanes, etc can be used as grinding aid components. The effect of grinding acceleration is achieved due to reducing of agglomeration and surface tension. The mass ratio of reactive silica to grinding aid
25 components can be varied from about 10:1 to about 10000:1.

The main idea of the mix proportioning is to create workable, dry or semi-dry complex admixture that meets the cost/benefit requirements and has significant improving influence on cement system properties. The presented mix design also provides protection against undesirable reaction between the complex
30 admixture components, mainly, due to high content of water reducer and small amount of water available for such reaction.

Any mixing process can be applied in the practice to meet the main requirement of composition homogenising. The promising results are

5 demonstrated by the high speed mixers (spindle or planetary type), vibrating mixers or mills, as well as the air jet mixers or mills. In case, if necessary, any types of the granulating equipment can be used for finishing of the complex admixture. The product as per the invention might be presented by wide range of coarse and fine granules. The quality the complex admixture can be improved by
10 drying, pressing, extrusion, crushing, calendering, etc. The required physical characteristics, as well as better homogenising of composition, necessary fineness and shape are achieved by means of such treatment.

The introduction of the complex admixture into cement or dry mix
15 production process allows to increase the compressive strength of these materials up to 145-
180 MPa. The cement composition can contain portland cement clinker including one or more combination of calcium silicates and/or calcium aluminates and one or more types of calcium sulfate, or portland cement with Blaine specific surface
20 area less than 400 m²/kg and the complex admixture. The mass ratio of portland cement to complex admixture can be varied from about 100:1 to about 2:1. The chemical composition of clinker and cement can vary in the limits of existing standards or special clinker and cement can be used. Generally, any kind of existing cements can be applied in this composition. (for example, in accordance
25 with ASTM C150, C595, C845, C91 or prEN197-1) This cements include, but are not limited by general use cements, moderate heat of hardening cements, high early strength cements, low heat cements, sulfate resisting cements, white portland cements, blended hydraulic cements, portland blast furnace slag cements, portland-pozzolan cements, special cements, expanding cements, high alumina
30 cements, oil-well cements, etc, as well as any combination and mix of this cements.

The large quantity up to 70% of mineral indigenous admixtures can be introduced in the cement composition. The natural materials as pozzolans, volcanic glasses, diatomaceous earth, perlite, tuff, volcanic pumice, natural sand,

5 quarts, marble, limestone, burnt gaize, burnt clay, burnt shale, rice husk ash,
bentonite, activated kaolin, etc and industrial by-products or wastes as granulated
blast furnace slag, fly ash, silica fume, catalytic and alum wastes, broken glass and
ceramic, calcium sulfate, etc can be used as mineral admixtures. Selection of
10 special mineral admixtures, for instance with high density, chemical, thermal or
abrasion resistance, thermal expansion, electric conductivity etc allow to produce
cement systems with specially designing and unique properties. The mass ratio of
mineral indigenous admixtures to complex admixture can be varied from about
100:1 to about 1:1. Maximum quantity of mineral admixtures in the cement
composition depends on type of mineral admixtures, as well as strength and
15 durability level required.

The dry mix can contain specially selected dry aggregates (for example, in
accordance with ASTM C387 or C33). The mass ratio of aggregates to total
cementing material (cement, mineral admixtures and complex admixture) can be
varied from about 10:1 to about 1:2.

20 The existing apparatus and technologies can be used for cement or dry mix
production process. Satisfactory results were achieved by the application of high
speed mixers (for dry mix or blended cement production), vibrating mixers or
mills, air jet mixers or mills, ball mills, tube ball mills (for cement production).
The mode of complex admixture introduction into portland cement - mineral
25 admixtures - aggregates systems covers all possible combinations. Adequately
formula was concluded in case if portland cement clinker and calcium sulfate (or
portland cement as component) and the complex admixture was interground in
mill (preferable, open cycle ball mill). The product in accordance with the formula
is presented by modified super high strength cement, which can be used as final
30 product or for consequent production of the blended cements (by inter grinding or
mixing with mineral admixtures) and dry mix (by mixing with aggregates). Joint
interground clinker (or portland cement) - mineral admixture - complex admixture
system also possessed high level of properties. Separate grinding of clinker and
mineral admixture components and consequent intergrinding or mixing with

- 5 complex admixture allows to design systems with very small water demand due to optimal and dense particles packing.

The concrete and mortars based on modified cements posses high strength and high durability, as well as excellent workability and pumping. The wide range of aggregates and fibrous materials (as polypropylene, nylon, glass) can be used
10 for concrete and mortars production. Introduction of the complex admixture as component of concrete mix is also possible, and for this case usage of pre-mixer is recommended. Good mixing effect is achieved if complex admixture, water and part of cement were pre-mixed in colloid mixer. Selection of special fillers and/or aggregates for concrete, for instance with high density, chemical, thermal or
15 abrasion resistance, thermal expansion, electric conductivity etc allow to design the wide range of concrete with special and unique properties.

The complex admixture modified cement paste, mortar or concrete based materials can be used after any kind of consequent treatment in fresh or hardening state. These treatment processes include, but are not limited by vibrating, pressing,
20 extrusion, calendering, drying, heat or autoclave treatment, etc. The required properties of products can be achieved by means of such treatment.

The invention can be described by the following examples which can explain the advantages of complex admixture application in cement and concrete technology and demonstrate the opportunity of production of the cement based
25 systems with unique properties. The examples are not intended to limit the scope of the invention. In what follows, "%" will mean "weight %", "ratio" will mean "weight ratio" and "parts" will mean "weight parts".

EXAMPLE 1

30

The example demonstrates the ability to raise the strength properties of normal portland cement based systems in case of complex admixture application for modifying of cement grinding process.

5 The complex admixture mix proportioning was the following:

Table 1

Type	Name	Specification	Composition
High Range Water Reducer	Sikament FF	35% Solid Content	3
Water Soluble Polymer	Mowilith-LDM2072		1
Low-Calcium Fly Ash	-	40% SiO ₂ Content	10
Condensed Silica Fume	-	90% SiO ₂ Content	10

10 The mixing of components in planetary mixer was continued during 5 minutes and after this procedure the complex admixture was presented by semi dry grainy particles with 0.5- 4 mm diameter. The produced admixture was used as modifier of cement grinding process. The composition was based on portland cement clinker, admixture and gypsum. The admixture amount was varied from 0 to 40% and the gypsum content was constant as 4% of clinker weight. The grinding media to total materials ratio was kept as 10:1 and grinding time was 1½

15 of hour. The properties of modified cements and dry mixes (at sand to cement ratio 1:1) in accordance with ASTM C348/C349/C387 are presented in Table 6. The test results indicate significant rise of the strength properties of modified cement systems at complex admixture content from 10 to 40 %.

20 EXAMPLE 2

The example demonstrates the ability to apply the complex admixture for the increasing of the early strength of blended cements containing 60% of blast furnace slag or fly ash.

25 The complex admixture mix proportioning was the following:

Table 2

Type	Name	Specification	Composition
SMF High Range Water Reducer	Melment-L10	35% Solid Content	3
Lightweight Perlite Sand	-	D _{max} = 1 mm	3
Hemi Water Gypsum	-	-	3
Rice Husk Ash	-	90% SiO ₂ Content	10

5

The mixing procedure was the same as per Example 1. The produced admixture was used as modifier of cement grinding process. The composition was based on 60% of blast furnace slag or fly ash, 35% portland cement and 5% of the admixture. The grinding equipment and conditions were the same as per Example 1 and grinding time was ½ of hour. The test results of modified cements and dry mixes (at sand to cement ratio 1:1) are presented in Table 6. The test results indicate significant rise of the early age strength of modified cement.

10

EXAMPLE 3

15

The example demonstrates the effect of the complex admixture to delay the setting of high strength cements.

The complex admixture mix proportioning was the following:

Table 3

Type	Name	Specification	Composition
Hyperplasticizer	Sikament-NN	40% Solid Content	15
Sulphate Na	-		1
Modified Lignosulphonate	Plastiment-BV40	30% Solid Content	1
Methyl Hydroxyethyl Cellulose	Tylose-MN	100% Powder	3
Silica Fume	-	90% SiO ₂ Content	50

20

The mixing procedure was the same as per Example 1. The produced admixture was used as modifier of cement grinding process. The composition was based on portland cement clinker and admixture. The admixture amount was varied from 5 to 10%. The grinding time was 1½ of hour. The test results of modified cements and dry mixes are presented in Table 6. The test results indicate significant delay of the high strength cement setting time.

25

5 EXAMPLE 4

The example demonstrates the ability to reduce the cement grinding time, as well as increase of the cement early strength.

The complex admixture mix proportioning was the following:

10 Table 4

Type	Name	Specification	Composition
SNF High Range Water Reducer	Sikament-FF	35% Solid Content	15
Calcium Formate	-	-	1
Triethanol Amine	-	15% Solid Content	1
Low-Calcium Fly Ash	-	40% SiO ₂ Content	50
Zeolite	-	50% SiO ₂ Content	50

The mixing procedure was the same as per Example 1. The produced admixture was used as modifier of cement grinding process. The cement composition and grinding conditions were the same as per Example 1. The admixture dosage was 5% and grinding time was 1 hour. The test results of modified cements and dry mixes are presented in Table 6. The test results indicate the reducing of the cement grinding time and increasing of the early age strength of modified cement.

20

EXAMPLE 5

The example demonstrates the possibility to design of the cement systems with special properties as super high strength, super low thermal expansion and high thermal resistance.

25

The complex admixture mix proportioning was the following:

Table 5

Type	Name	Specification	Composition
SNF High Range Water Reducer	Sikament NN	35% Solid Content	5
Zeolite	-	40% SiO ₂ Content	10
Condensed Silica Fume	-	90% SiO ₂ Content	10

5

The mixing procedure was the same as per Example 1. The produced admixture was used as modifier of cement grinding process. The normal portland cement was replaced by 45% of fine pulverised (Blaine specific surface area of 350 m²/kg) powder of Li-Si-Al-O-N glass brakeage that is a glass factory by-product as low thermal expansion filler and by 25% of the admixture (the portland cement content was 30% of total amount). The grinding equipment and conditions were the same as per Example 1 and grinding time was ½ of hour. The test results of dry mixes (at special sand to cement ratio 1:1) are presented in Table 6. The Li-Si-Al-O-N glass and ZnO-Al₂O₃-SiO₂ based ceramic brakeage are used as special sand in the dry mixes. The test results demonstrate the possibility to produce the cement systems with super high compressive strength up to 180 MPa and around 250 MPa after low temperature (150-450 °C) burning, super low thermal expansion coefficient up to 10⁻⁶ °C⁻¹ and high thermal resistance up to 750 °C.

20 EXAMPLE 6

The example demonstrates the opportunity to produce wide range of the dry mix products based on high strength cement as per Example 1. The high strength cement containing 20% of the complex admixture was used. The test results of dry mixes at sand to cement ratio 1, 3, 5, 7, 10 are presented in Table 6. The test results confirm the ability to produce the super high strength dry mixes with compressive strength up to 145 MPa, high strength dry mixes (compressive strength 40-65 MPa) for wide scale applications, as well as very cheap normal grade dry mixes with sand content from 7 to 10 parts per 1 part of the high strength cement.

5 EXAMPLE 7

The example demonstrates the ability to produce super high strength concrete based on the complex admixture as per Example 1. The normal portland cement and the complex admixture at 40% content in total binder were used. The complex admixture and cement are pre-mixed with water in colloid mixer in order to produce activated fluid system. The admixture to cement ratio 1:1 and total amount of water have been used. The admixture-and-cement fluid pre-mix was used for concrete production immediately after activation. The mixture proportion and test results of concrete are presented in Table 7. The test results confirm the ability to produce the super high strength concrete with compressive strength up to 165 MPa.

Table 6. - Complex Admixture Based Cement Proportion and Properties

No	Cement Mixture Proportions, %					Specific Surface Area, m2/kg	Setting Time, h:min		Cement Sand	W/C	Flexural Strength, MPa @				Compressive Strength, MPa @			
	Clinker	Gypsum	Admixtur e	Slag	Fly Ash		Initial	Final			1 day	3 days	7 days	28 days	1 day	3 days	7 days	28 days
1.1.1	96	4	0	0	0	320	1:50	2:30	1 : 2.75	0.45	2.1	6.1	6.9	7.9	15.1	36.2	42.0	56.1
1.1.2	96	4	0	0	0	320	1:50	2:30	1 : 1.00	0.30	2.8	8.2	9.3	10.5	25.2	60.5	51.4	82.5
1.2.1	94	4	2	0	0	360	1:45	2:25	1 : 2.75	0.42	2.2	6.4	7.3	8.2	18.9	45.2	38.4	61.7
1.2.2	94	4	2	0	0	360	1:45	2:25	1 : 1.00	0.27	3.3	9.6	10.9	12.3	27.5	65.9	56.0	89.9
1.3.1	86	4	10	0	0	750	1:35	2:15	1 : 2.75	0.35	2.5	7.3	8.2	9.3	26.0	62.4	53.0	85.1
1.3.2	86	4	10	0	0	750	1:35	2:15	1 : 1.00	0.21	3.9	11.3	12.8	14.5	36.9	88.5	75.2	120.7
1.4.1	82	3	20	0	0	950	1:30	2:10	1 : 2.75	0.29	2.7	7.7	8.8	9.9	24.8	59.5	50.5	81.1
1.4.2	82	3	20	0	0	950	1:30	2:10	1 : 1.00	0.18	4.0	11.6	13.2	14.9	41.2	98.7	83.9	134.6
1.5.1	77	3	30	0	0	1150	1:25	2:05	1 : 2.75	0.25	2.8	8.1	9.2	10.4	27.2	65.2	55.4	88.9
1.5.2	67	3	30	0	0	1150	1:25	2:05	1 : 1.00	0.16	4.1	12.0	13.6	15.4	43.3	103.7	88.1	141.4
1.6.1	58	2	40	0	0	1350	1:20	2:00	1 : 2.75	0.22	4.4	7.7	10.3	11.9	28.5	62.6	74.1	94.4
1.6.2	58	2	40	0	0	1350	1:20	2:00	1 : 1.00	0.14	6.8	12.3	14.9	18.9	45.2	83.8	111.2	148.2
2.1.1	34	1	5	60	0	525	2:30	3:15	1 : 2.75	0.30	3.8	6.9	7.2	10.8	27.2	50.5	56.4	93.8
2.1.2	34	1	5	60	0	525	2:30	3:15	1 : 1.00	0.23	3.9	7.1	12.5	13.8	38.9	72.2	65.0	112.5
2.2.1	34	1	5	0	60	555	2:45	3:45	1 : 2.75	0.33	2.3	4.2	5.4	8.3	12.2	22.6	41.4	59.5
2.2.2	34	1	5	0	60	555	2:45	3:45	1 : 1.00	0.23	2.9	5.2	8.4	9.7	18.6	34.4	58.6	88.5
3.1.1	95	0	5	0	0	500	2:15	2:45	1 : 2.75	0.31	3.4	6.2	10.0	9.5	18.3	34.0	57.9	87.4
3.1.2	95	0	5	0	0	500	2:15	2:45	1 : 1.00	0.19	4.5	8.1	13.2	11.4	25.4	47.1	80.3	121.3
3.2.1	90	0	10	0	0	675	2:55	4:00	1 : 2.75	0.25	4.5	8.2	13.3	11.5	19.1	35.4	60.4	91.2
3.2.2	90	0	10	0	0	675	2:55	4:00	1 : 1.00	0.15	6.0	10.9	17.6	15.2	29.4	54.6	93.0	140.4
4.1.1	91	4	5	0	0	485	1:35	2:10	1 : 2.75	0.32	3.6	6.5	10.5	9.1	13.7	25.4	43.3	65.4
4.1.2	91	4	5	0	0	485	1:35	2:10	1 : 1.00	0.21	4.3	7.8	12.6	10.9	19.4	36.0	61.4	92.7
5.1.1	29	1	25	45	0	460	1:40	2:20	1 : 1.00	0.15	6.5	12.9	18.3	25.2	46.4	98.7	146.4	180.7
5.1.2	29	1	25	45	0	460	1:40	2:20	1 : 1.00	0.15	6.3	11.7	16.5	20.4	42.9	91.2	134.5	175.1
6.1.1	58	2	40	0	0	950	1:30	2:10	1 : 1.00	0.15	6.8	12.3	14.9	18.9	45.2	83.8	111.2	148.2
6.1.2	58	2	40	0	0	950	1:30	2:10	1 : 3.00	0.25	4.2	7.3	9.9	11.7	27.9	51.7	68.6	91.4
6.1.3	58	2	40	0	0	950	1:30	2:10	1 : 5.00	0.35	3.4	5.9	8.0	9.4	23.4	43.3	57.5	76.6
6.1.4	58	2	40	0	0	950	1:30	2:10	1 : 7.00	0.45	2.9	5.1	6.9	8.2	18.5	34.4	45.6	60.8
6.1.5	58	2	40	0	0	950	1:30	2:10	1 : 10.00	0.55	2.5	4.4	6.0	7.1	10.6	19.6	26.0	34.6

Table 7. - Complex Admixture Based Concrete Proportion and Properties

Concrete Mixture Proportions, kg/m ³					Slump, mm	Compressive Strength, MPa @					
Cement	Admixture	Water	Sand	Coarse Aggregate		W/(C+A)	1 day	3 days	7 days	28 days	90 days
520	130	130	420	1200	200	0.2	45	85	120	155	165

CLAIMS

What is claimed is:

- 5 1. A dry or semi- dry complex admixture for cement systems containing water reducer or high range water reducer in aqueous solution and active silicon dioxide based sorbent, wherein
 - a sorbent is presented by fine alkali reactive non-crystalline silica dioxide based materials as fly ash, rice husk ash, zeolite, silica fume,
10 bentonite, activated kaolin, montmorillonite, diatomaceous earth;
 - a sulphonated melamine, naphthalene formaldehyde, polyacrylate based admixtures, or their mix (including other admixtures) are used as high range water reducer;
 - the mass ratio of reactive silica dioxide component to water reducer is
15 ranged from about 5:1 to about 100:1.
2. A complex admixture composition according to Claim 1, wherein the high porous light weight sand is used as water accumulating component of active sorbent.
3. A complex admixture composition according to Claims 1-2, wherein volcanic
20 pumice, tuff, expanded clay, expanded perlite, expanded slag, expanded glass is used as accumulating porous component.
4. A complex admixture composition according to Claims 1-3, wherein the mass ratios of reactive silica to accumulating porous component can be varied from about 10:1 to about 1:1.
- 25 5. A complex admixture composition according to Claims 1-4, wherein the non-organic or organic salts or hydroxides of metals are used as electrolytic agent of active sorbent.
6. A complex admixture composition according to Claims 1-5, wherein the metal (especially, alkali and alkali earth) aluminates, hydroxides and/or carbonates,

as well as sodium nitrite, sulphate Al, Na, K, Ca, calcium chloride, calcium formate are used as electrolytic agent.

7. A complex admixture composition according to Claims 1-6, wherein the mass ratio of reactive silica component to electrolytic agent is varied from about 10:1 to about 1000:1.
8. A complex admixture composition according to Claims 1-7, wherein the low-, hemi- and non- water salts or combinations that are able to combine with water are used as water combining component of active sorbent.
9. A complex admixture composition according to Claims 1-8, wherein the one or more types of calcium sulfate, high alumina cement or sulphate Na is used as water combining component.
10. A complex admixture composition according to Claims 1-9, wherein the mass ratios of reactive silica to water combining component is adjusted from about 1:1 to about 100:1.
11. A complex admixture composition according to Claims 1-10, wherein the water-soluble polymer is used as component of complex admixture.
12. A complex admixture composition according to Claims 1-11, wherein the polyvinyl alcohol, polyvinyl acetate, polyacrylamide, cellulose ethers, methylcellulose, carboxymethyl cellulose, hydroxyethyl cellulose is applied as water-soluble polymer.
13. A complex admixture composition according to Claims 1-12, wherein the mass ratio of reactive silica to water soluble polymer is varied from about 3:1 to about 100:1.
14. A complex admixture composition according to Claims 1-13, wherein the retarder of hydration, setting, and/or hardening of cement system is used as component of complex admixture.
15. A complex admixture composition according to Claims 1-14, wherein lignosulphonates, sugars, hydroxycarbonic acids and their salts, carboxylates, phosphonic or phosphoric acids, as well as their ethers and salts are used as the retarders.

16. A complex admixture composition according to Claims 1-15, wherein the mass ratio of reactive silica to retarder is chosen from about 50:1 to about 1000:1.
17. A complex admixture composition according to Claims 1-16, wherein the air detraining, hydrophobic, air entraining, foaming and/or gas creating admixtures are applied as structure formation components of the main composition.
18. A complex admixture composition according to Claims 1-17, wherein the three- butyl phosphate is used as air detraining component.
19. A complex admixture composition according to Claims 1-18, wherein the silicon based compounds containing silicones, silanes, silanols and/or siloxanes groups as alkyl alkoxy silanes are used as hydrophobic components.
20. A complex admixture composition according to Claims 1-19, wherein the neutralised hydroaromatic and fatty carboxylic acid, tall oil, vinsol resin and protein-based admixtures are used as air entraining or foaming agents.
21. A complex admixture composition according to Claims 1-20, wherein the metal (as aluminium) powder, hydrogen peroxide are applied as gas creating component.
22. A complex admixture composition according to Claims 1-21, wherein the mass ratio of reactive silica to structure formation components can be varied from about 10:1 to about 10000:1.
23. A complex admixture composition according to Claims 1-22, wherein the grinding aid components is used as component of complex admixture.
24. A complex admixture composition according to Claims 1-23, wherein the triethanol amine, amine acetate salts, EDTA, acetic acid, hydrocarbons, silanes, methyl chlorine or fluorine silane are applied as grinding aid components.
25. A complex admixture composition according to Claims 1-21, wherein the mass ratio of reactive silica to grinding aid components can be varied from about 10:1 to about 10000:1.

26. A dry or semi- dry complex admixture production process including mixing of components according to Claims 1-25.
27. A complex admixture production process according to Claims 26, wherein the high speed mixer spindle or planetary type, vibrating mixers or mills, as well as the air jet mixers or mills are used.
28. A complex admixture production process according to Claims 26-27, wherein the additional granulating, drying, pressing, extrusion, crushing, calendering process is applied for finishing the composition.
29. A cement composition that includes
- the complex admixture according to Claim 26-28 and
 - portland cement clinker based on one or more combination of calcium silicates and/or calcium aluminates and one or more types of calcium sulfate, and/or
 - portland cement as general use cements, moderate heat of hardening cements, high early strength cements, low heat cements, sulfate resisting cements, white portland cements, blended hydraulic cements, portland blast furnace slag cements, portland-pozzolan cements, special cements, expanding cements, high alumina cements, oil-well cements, as well as any combination and mix of this cements.
30. A cement according to Claim 29, wherein the mass ratio of portland cement component to complex admixture is varied from about 100:1 to about 2:1.
31. A cement composition according to Claims 29-30, wherein the mineral admixtures are introduced in the cement composition.
32. A cement composition according to Claims 31, wherein the pozzolans, volcanic glasses, diatomaceous earth, perlite, tuff, pumice, natural sand, quartz, marble, limestone, burnt gaize, burnt clay, burnt shale, rice husk ash, bentonite, activated kaolin, granulated blast furnace slag, fly ash, silica fume, catalytic and alum wastes, broken glass, broken ceramic, calcium sulfate are used as mineral admixtures.

33. A cement composition according to Claims 31-32, wherein the mass ratio of mineral admixtures to complex admixture is varied from about 100:1 to about 1:1.
34. A cement production process that includes the grinding or mixing of components according to Claims 29-33.
35. A cement production process according to Claim 34, wherein the separate grinding of portland cement and mineral admixture components and consequent intergrinding or mixing with the complex admixture is applied.
36. A cement production process according to Claims 34-35, wherein the high speed mixers, vibrating mixers or mills, air jet mixers or mills, ball mills, tube ball mills are applied.
37. A dry mix composition that includes the portland cement and dry aggregates and the complex admixture according to Claim 26-28.
38. A dry mix composition that includes the cement according to Claim 34-36 and dry aggregates.
39. A dry mix composition according to Claims 37-38, wherein the mass ratio of aggregates to total cementing materials (cement, mineral admixtures and complex admixture) is varied from about 10:1 to about 1:2.
40. A dry mix production process that includes the mixing of components according to Claims 37-39.
41. A dry mix production process according to Claim 40, wherein the high speed mixers, vibrating mixers, air jet mixers are used.
42. A concrete and mortars based on modified cement or dry mix according to Claims 34-36, 40-41.
43. A concrete and mortar that includes the portland cement and aggregates and the complex admixture according to Claims 26-28.
44. A cement, dry mix, mortar and/or concrete according to Claim 34-36, 40-43 that includes the special fillers and/or aggregates with high density, chemical, thermal or abrasion resistance, thermal expansion, electric conductivity and/or fibrous materials as polypropylene, nylon, glass.

45. A cement paste, mortar and/or concrete modified by the complex admixture according to Claims 29-44 are used after vibrating, pressing, extrusion, calendering, drying, heat or autoclave treatment.
- 5 46. The complex admixture composition and/or the mode of production in accordance with Claims and/or including any references on Examples.
47. The high compressive strength of 70-180 MPa cement, dry mix, mortar and/or concrete composition and/or the mode of production in accordance with Claims and/or including any references on Examples.
- 10 48. The cement, dry mix, mortar and/or concrete composition with high volume of 15-70% of mineral admixtures in cement content and/or the mode of production in accordance with Claims and/or including any references on Examples.
49. The cement, dry mix, mortar and/or concrete composition and/or the mode of production in accordance with Claims including any references on Examples.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/TR 98/00008

A. CLASSIFICATION OF SUBJECT MATTER

IPC⁶: C 04 B 28/02, 24/24, 18/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC⁶: C 04 B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

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C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 275 652 A (DASTOL) 04 January 1994 (04.01.94), totality.	1-49
A	US 5 466 289 A (YONEZAWA et al.) 14 November 1995 (14.11.95), totality, (cited in the application)	1-49
A	EP 0 184 346 A1 (MITSUBISHI YUKA FINE CHEMICALS CO. LTD.) 11 June 1986 (11.06.86), totality.	1-49
A	WO 85/00 359 A1 (RESEARCH ONE LIMITED PARTNERSHIP) 31 January 1985 (31.01.85), totality.	1-49

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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Date of the actual completion of the international search

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Beck

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/TR 98/00008

Im Recherchenbericht angeführtes Patentdokument Patent document cited in search report Document de brevet cité dans le rapport de recherche		Datum der Veröffentlichung Publication date Date de publication	Mitglied(er) der Patentfamilie Patent family member(s) Membre(s) de la famille de brevets	Datum der Veröffentlichung Publication date Date de publication	
US A	5275452	04-01-94	AT A	4276/83	15-03-87
			AT B	384206	12-10-87
			AU A1	22159783	14-06-84
			AU B2	548300	05-12-85
			BE A1	898398	30-03-84
			BR A	8306701	17-07-84
			CA A1	1220792	21-04-87
			CH A	658854	15-12-86
			DD A5	212954	29-08-84
			DE A1	3343948	07-06-84
			DE C2	3343948	18-02-88
			DK A0	560378	05-12-84
			DK A	560378	08-06-84
			DK B	165783	18-01-94
			DK C	165783	14-06-84
			ES A1	527825	13-06-85
			ES A5	527825	16-07-85
			ES A1	8505904	16-10-85
			FI A0	834404	01-12-84
			FI A	834404	08-06-84
			FI B	729622	30-04-87
			FI C	729622	10-08-87
			FR A1	2537137	08-06-84
			FR B1	2537137	06-12-91
			GB A0	8332361	11-01-84
			GB A1	2213140	20-06-84
			GB B2	2213140	17-09-86
			IT A0	8323918	28-11-86
			IT A	116727	13-05-87
			JP A2	9111196	28-06-84
			JP B4	1035789	27-07-89
			MX A	157587	02-12-88
			NL A	8304193	02-07-84
			NL B	1905500	16-11-93
			NL C	1905500	18-04-94
			NO A	8241000	28-08-84
			NO B	153566	06-01-86
			NZ A	206493	11-07-86
			PH A	199438	14-08-86
			PL A1	244938	24-08-84
			PT A	77741	01-12-84
			PT B	77741	16-04-86
			SE A0	8306700	05-12-84
			SE A	8306700	08-06-84
			SE B	460288	25-09-89
			ZA A	8308678	31-07-85
			US A	5472501	05-12-85
US A	5466289	14-11-95	JP B2	2646449	27-08-97
			CA A2	2107268	31-03-94
			JP A2	6191918	12-07-94
EP A1	184346	11-06-86	DE C0	3572797	12-10-89
			EP B1	184346	06-09-89
			JP A2	61122146	10-06-86
			JP B4	1057070	04-12-89
			US A	4684407	04-08-87
WD A1	8500359	31-01-85	AU A1	31542/84	07-02-85
			BR A	8406962	11-06-85
			CA A1	1218387	24-02-87
			EP A1	148935	24-07-85
			IL A0	722229	31-10-84
			IL A1	722229	20-12-87
			IT A0	8421681	29-06-84
			IT A	1214471	19-01-80
			JP T2	60501707	11-10-85
			US A	4505753	19-03-85
			ZA A	8404882	28-05-86